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PHOTOSENSITIVE PLANOGRAPHIC PRINTING PLATE

[Kankosei Heiban Insatsu Ban]

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Specification

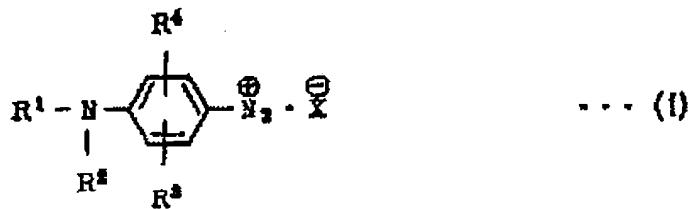
1. Title of the invention

PHOTOSENSITIVE PLANOGRAPHIC PRINTING PLATE

2. Patent Claims

1. A photosensitive planographic printing plate with the following characteristics: In a photosensitive planographic printing plate obtained by configuring a photosensitive layer which includes a diazo resin above an aluminum sheet in possession of an anodic oxidation layer which has been formed as a result of an anodic oxidation treatment within either phosphoric acid or an electrolytic solution inclusive of phosphoric acid as a main component and the average pore diameter and pore density of which fall respectively into ranges of 200 ~ 900 Å and 100 ~ 1,000 N/μm²,

Said diazo resin is a diazo resin obtained by coupling, with a polymer which includes a carboxylic acid residue or carboxylic anhydride residue, a diazo compound expressed by the following general formula I:



¹ Numbers in the margin indicate pagination in the foreign text.

(In the formula, R^1 signifies an alkyl group, alkenyl group, aryl group, or aralkyl group which includes at least one hydroxyl group, whereas R^2 signifies a hydrogen atom, alkyl group, alkenyl group, aryl group, or aralkyl group, whereas R^3 and R^4 , which may be mutually identical or different, each signify a hydrogen atom, alkyl group, or alkoxy group, whereas X^- signifies an anion).

2. A photosensitive planographic printing plate specified in Claim 1 wherein R^3 and R^4 in said general formula I are each hydrogen atoms.

3. A photosensitive planographic printing plate specified in Claim 1 wherein R^1 in said general formula I is a 2-hydroxyethyl group.

4. A photosensitive planographic printing plate specified in Claim 1 wherein R^1 in said general formula I is a 2-hydroxyethyl group and wherein R^2 is an ethyl group).

5. A photosensitive planographic printing plate specified in Claim 1 wherein X^- is PF_4^- or BF_4^- .

3. Detailed explanation of the invention

(Industrial application fields)

The present invention concerns a photosensitive planographic printing plate. More specifically, it concerns a photosensitive planographic printing plate characterized by a high printing force resistance, favorable preservation stability & erasability, and favorable exposure image visualization potential /2

& image reproducibility. More precisely, it concerns a photosensitive planographic printing plate which entails a minimal fog and a favorable operative efficiency even in a case where it is handled underneath a white beam lamp.

(Prior art)

Diazo resins obtained by reacting aromatic diazonium salts (e.g., diphenylamine-4-diazonium salt) and active carbonyl compounds (e.g., formaldehyde, etc.) have publicly been known in the prior art. In the field of printing, in particular, diazo resins are being used extensively as platemaking photosensitive materials for offset printing planographic plates based on the variations of their solubilities as a result of photodecomposition.

An offset printing plate can be obtained by mixing a diazo resin with a binder, etc. and by coating the obtained mixture on a hydrophilic metal, paper, etc., preferably on aluminum. In a case where this plate is exposed imagewise, its exposed portion becomes cured and insoluble with a development solution, and thus, in a case where it is treated with the development solution, hydrophilic and hydrophobic segments become formed on the printing plate, and it can be used for printing by using water and a fatty ink.

Since the diazo resins exert immense effects on printing plates, they have been variously investigated. Organic salts such as organic sulfonates, etc., for example, are mentioned as anions

of diazo groups in Japanese Patent Publication Kokoku No. Sho 47[1972]-1167 Gazette and the specification of U.S. Patent No. 3,300,309, but they are flawed in that the user friendliness is questionable, for visualized planes are difficult to view during exposure. Japanese Patent Application Publication Kokai No. Sho 54[1979]-98613 Gazette notes inorganic salts such as halogenated Lewis acid salts, etc. as anions of diazo groups, and although images can be favorably visualized during exposure, the preservation stability may, depending on certain polymer combinations, not be satisfactory under severe conditions of high temperature and high humidity.

In consideration of the operative efficiency, etc., on the other hand, it has become very urgent to enhance the sensitivities of printing plates in recent years, and various investigations have been conducted in the field of diazo photosensitive materials as well.

In a case where a diphenylamine-4-diazonium salt and a carbonyl ceramic are polycondensed, for example, a diazo compound with a high sensitivity can be obtained by optimally selecting the reaction molar ratio, reaction conditions, etc., although the developability and preservation stability are questionable.

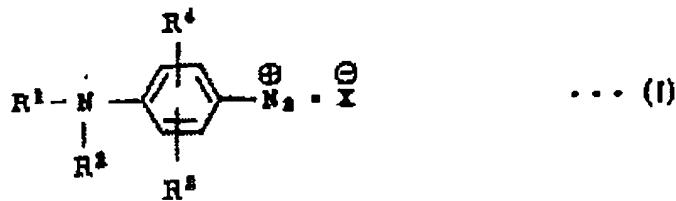
The condensation product of diphenylamine and formaldehyde, furthermore, is endowed with a secondary absorption within a visible region of 420 ~ 500 nm, and since it absorbs and decomposes the beams within this wavelength range, it is extremely

difficult to handle underneath a white beam lamp, which represents a grave shortcoming from the standpoints of production and use.

Novel diazo photosensitive materials other than this condensation product of diphenylamine and formaldehyde have also been investigated (Japanese Patent Application Publication Kokai Nos. Sho 54[1979]-30121, Sho 58[1983]-127923, and Sho 58[1983]-62641). Japanese Patent Application Publication Kokai No. Sho 54[1979]-30121 Gazette mentions a diazo compound which includes a polyester group as a principal chain, but it is necessary to use such reagents as trifluoroacetic acid, etc. as a solvent, and furthermore, the reaction conditions are practically difficult to establish, for they mandate a high temperature and a long period.

The novel diazo compound mentioned in the respective Gazettes of Japanese Patent Application Publication Kokai Nos. Sho 58[1983]-62641 and Sho 58[1983]-127923, on the other hand, permits improved reaction conditions, but it involves large numbers of convoluted synthesis processes. The developability of the obtained novel diazo compound, furthermore, is inferior, due to which its quantitative ratio added to a photosensitive layer becomes limited.

The present inventors previously discovered that, in a case where a diazo resin obtained by coupling, with a polymer which includes a carboxylic acid residue or carboxylic anhydride residue, a diazo compound expressed by the following general formula I:



(In the formula, R¹ signifies an alkyl group, alkenyl group, aryl group, or aralkyl group which includes at least one hydroxyl group, whereas R² signifies a hydrogen atom, alkyl group, alkenyl group, aryl group, or aralkyl group, whereas R³ and R⁴, which may be mutually identical or different, each signify a hydrogen atom, alkyl group, or alkoxy group, whereas X⁻ signifies an anion), a photosensitive planographic printing plate endowed with a high sensitivity and favorable developability & exposure image visualization potential can be obtained (Japanese Patent Application Tokugan No. Sho 60[1985]-114393). /3

(Problems to be solved by the invention)

It was, however, unsatisfactory in terms of printing force resistance and image reproducibility.

One objective of the present invention is therefore to provide a photosensitive planographic printing plate characterized by an improved image reproducibility and a high printing force resistance.

Another objective of the present invention is to provide a photosensitive planographic printing plate characterized by favorable developability & exposure image visualization potential.

Still another objective of the present invention is to provide a photosensitive planographic printing plate which

exhibits favorable preservation stability & erasability and which entails a minimal fog and a favorable operative efficiency even in a case where it is handled underneath a white beam lamp.

(Mechanism for solving the problems)

To synopsize the present invention, the present invention represents an invention concerning a photosensitive planographic printing plate, and it is characterized as follows: In a photosensitive planographic printing plate obtained by configuring a photosensitive layer which includes a diazo resin above an aluminum sheet in possession of an anodic oxidation layer which has been formed as a result of an anodic oxidation treatment within either phosphoric acid or an electrolytic solution inclusive of phosphoric acid as a main component and the average pore diameter and pore density of which fall respectively into ranges of 200 ~ 900 Å and 100 ~ 1,000 N/μm²,

Said diazo resin is a diazo resin obtained by coupling, with a polymer which includes a carboxylic acid residue or carboxylic anhydride residue, the aforementioned diazo compound expressed by the general formula I.

In the following, the present invention will be concretely explained.

The diazo resin of the present invention is obtained by esterifying, with a polymer which includes a carboxylic acid residue or carboxylic anhydride residue, a diazo compound in

possession of a hydroxyl group expressed by the aforementioned general formula I.

The esterifying reaction may be induced in compliance with conventionally-known methods (e.g., Sandler Karo, *Organic Functional Group Preparation*, published by Academic Press, 1968, Vol. 1, etc.).

In such a case, the degree of esterification can be freely controlled by varying the feeding ratio of the diazo compound (I). The balance of various performances such as developability, exposure image visualization potential, etc. can be freely adjusted by varying said feeding ratio and by thus varying the degree of esterification. The introduction rate of the diazo compound (I) is designated within a range of 10% ~ 95%, preferably 15 ~ 90%.

As far as the present invention is concerned, furthermore, the anion of the diazo compound introduced to the polymer may be substituted with another desired anion in accordance with an ordinary method.

Ones expressed by the aforementioned general formula I are conceivable as such diazo compounds.

In the formula, R^1 is concretely instantiated by a 2-hydroxyethyl group, 1-hydroxyethyl group, hydroxymethyl group, 1,2-dihydroxyethyl group, hydroxyphenyl group, hydroxytoluyl group, hydroxyxylyl group, hydroxybenzyl group, hydroxystyryl group, hydroxycinnamyl group, hydroxynaphthyl group, etc.

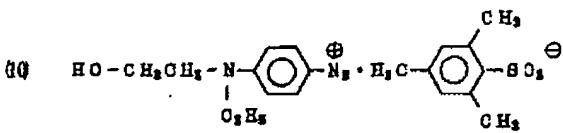
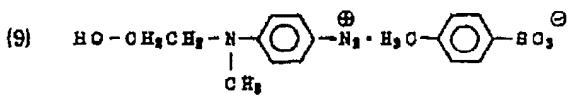
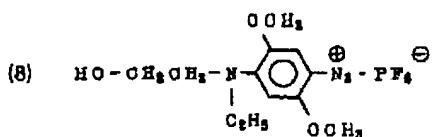
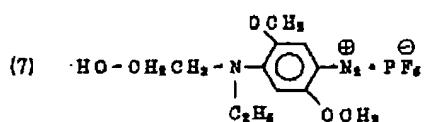
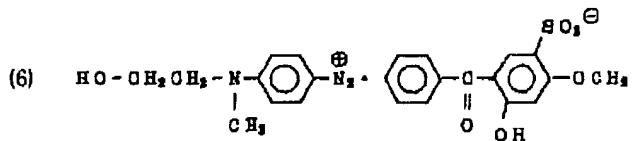
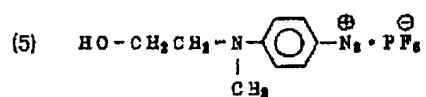
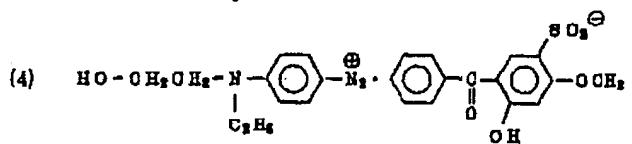
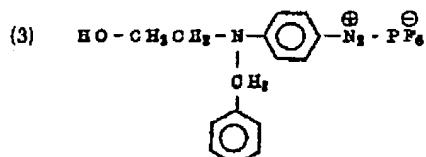
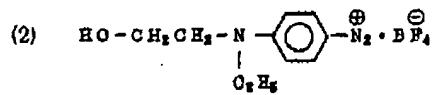
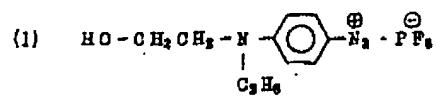
R^2 is concretely instantiated by a methyl group, ethyl group, propyl group, vinyl group, allyl group, phenyl group, benzyl group, etc.

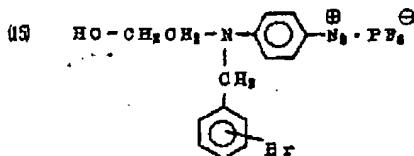
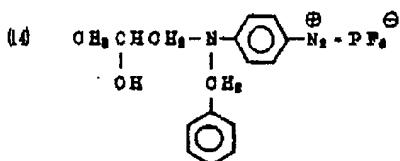
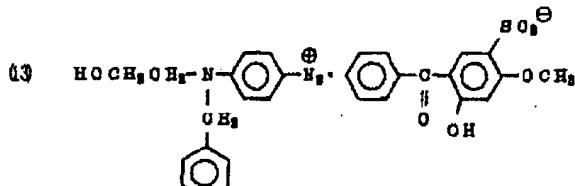
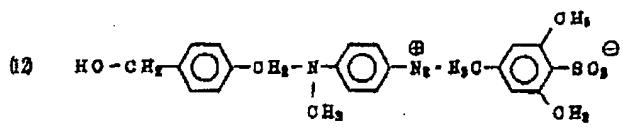
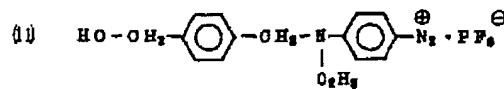
R^3 and R^4 are each concretely instantiated by a methyl group, ethyl group, propyl group, methoxy group, ethoxy group, etc.

X^- is concretely instantiated by organic carboxylic acids such as decanic acid, benzoic acid, etc., organic phosphoric acids such as phenylphosphoric acid, etc., and sulfonic acids, which are representatively instantiated by aliphatic and/or aromatic sulfonic acids such as methanesulfonic acid, chloroethanesulfonic acid, dodecanesulfonic acid, benzenesulfonic acid, toluenesulfonic acid, mesitylenesulfonic acid & anthraquinonesulfonic acid, 2-hydroxy-4-methoxybenzophenone-[5]-sulfonic acid, hydroquinonesulfonic acid, 4-acetylbenzenesulfonic acid, dimethyl 5-sulfoisophthalate, etc., hydroxyl group-containing aromatic compounds such as 2,2',4,4'-tetrahydroxybenzophenone, 1,2,3-trihydroxybenzophenone, 2,2',4-trihydroxybenzophenone, etc., halogenated Lewis acids such as hexafluorophosphoric acid, tetrafluoroboric acid, $ZnCl^-$, etc., and perhalogenic acids such as ClO_4^- , IO_4^- , etc.

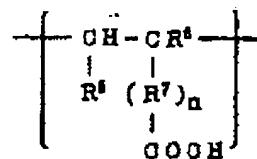
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Of the diazo compounds expressed by the aforementioned general formula I, representative compounds will be listed below, although the present invention is not limited by them.

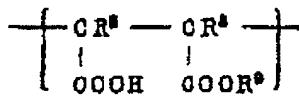




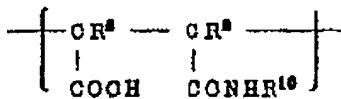
The polymer which includes a carboxylic acid residue or carboxylic anhydride residue may, for example, be instantiated by polymers which possess constituent units expressed by the following formulae II ~ V; polymers which possess constituent units derived from itaconic acid, its half esters, and/or its anhydride; acidic cellulose derivatives; acidic vinyl alcohol; etc.:



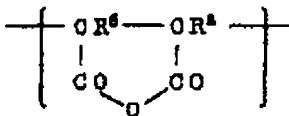
... (II)



... (III)



... (IV)



... (V)

(In the formulae, R^{5} and R^{8} each signify a hydrogen atom or alkyl group (e.g., alkyl groups

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which contain 1 ~ 8 carbon atoms), whereas R^{6} signifies a hydrogen atom, methyl group, alkylamido group, aralkylamido group, or arylamido group (e.g., propylamido group, hexylamido group, nonylamido group, phenylamido group, p-hydroxyphenylamido group, and benzylamido group), whereas R^{7} signifies either a phenylene group or alkylene group which contains 1 ~ 7 carbon atoms and which may optionally possess a hydroxyl group (e.g., hydroxymethylene group, methylene group, ethylene group, butylene group, and heptylene group), whereas R^{9} signifies a hydrogen atom, an alkyl or cycloalkyl group which may optionally be substituted with a substituent(s) such as a hydroxy group, acryloyl group, methacryloyl group, phenyl group, etc. (e.g., hydroxyethyl group, benzyl group, cyclohexyl group, and cyclopentyl group), or an aryl group (e.g., phenyl group, toluyl group, and p-hydroxyphenyl

group), whereas R^{10} signifies an alkyl group which may optionally be substituted with a substituent(s) such as a hydroxyl group, phenyl group, etc. (e.g., amyl group, dodecyl group, hydroxyethyl group, benzyl group, and allyl group), an aryl group (e.g., phenyl group, p-hydroxyphenyl group, and toluyl group), or a cycloalkyl group (e.g., cyclohexyl group and cyclopentyl group), whereas n signifies 0 or 1).

Compounds which yield the constituent units expressed by the aforementioned formula II may, for example, be instantiated by acrylic acid, methacrylic acid, crotonic acid, itaconanilic acid, oleic acid, vinylacetic acid vinylglycolic acid, vinylbenzoic acid, etc.

Compounds which yield the constituent units expressed by the aforementioned formula III may, for example, be instantiated by maleic acid, maleic acid monoalkyl esters, maleic acid monohydroxyalkyl esters, maleic acid monobenzyl ester, maleic acid monophenyl ester, maleic acid monocyclohexyl ester, fumaric acid or its half ester, citraconic acid or its half ester, etc.

Compounds which yield the constituent units expressed by the aforementioned formula IV may, for example, be instantiated by maleic acid monoalkylamides, maleic acid monohydroxyalkylamides, maleic acid monobenzylamide, maleic acid monophenylamide, citraconic acid monoalkylamides, citraconic acid monophenylamide, etc.

Compounds which yield the constituent units expressed by the aforementioned formula V may, for example, be instantiated by maleic anhydride, citraconic anhydride, etc.

Itaconic acid, its half esters, and its anhydride are instantiated by itaconic acid, itaconic acid monoalkyl esters, itaconic acid monobenzyl ester, itaconic acid monophenoxyethyl ester, itaconic acid monophenyl ester, itaconic acid monocyclohexyl ester, itaconic anhydride, etc.

The acidic cellulose derivatives may, for example, be instantiated by cellulose acetate phthalate, hydroxypropylmethyl cellulose phthalate, hydroxypropylmethyl cellulose hexahydrophthalate, etc.

The acidic polyvinyl alcohols, furthermore, are instantiated by a vinyl alcohol-vinyl phthalate copolymer, vinyl acetate-vinyl alcohol-vinyl phthalate copolymer, etc.

Of the aforementioned formulae II ~ V, ones represented by V are especially desirable in that they can be synthesized with ease. A hydrogen atom or methyl group, furthermore, is desirable as R¹ and R².

The polymer of the present invention that includes a carboxylic acid residue or carboxylic anhydride residue can be synthesized by homopolymerizing or copolymerizing compounds which yield the aforementioned respective constituent units in accordance with conventionally-known methods.

There are no special restrictions on copolymerized components so long as they can be copolymerized with the respective monomers

of II ~ V. They are concretely instantiated by styrenes, acrylic acid esters, methacrylic acid esters, vinyl ethers, acrylamides, methacrylamides, vinyl ketones, olefins (e.g., ethylene, propylene, etc.), and vinyl esters as well as N-vinylpyrrolidone, N-vinylcarbazole, 4-vinylpyridine, acrylonitrile, methacrylonitrile, etc.,

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although it is also possible select others so long as they can be copolymerized. It is desirable for the ratio of the copolymerized component(s) to be designated within a range of 10 mol% ~ 90 mol%, preferably 15 mol% ~ 85 mol%.

One the average molecular weight of which falls into a range of 1,000 ~ 100,000, preferably 2,000 ~ 50,000, is normally used as the polymer of the present invention.

In the context of manufacturing a planographic printing plate, for example, the photosensitive diazo resin of the present invention may be used alone, although it may also be used as mixtures with various other synthetic resins. It may, for example, be advantageously mixed with a lipophilic polymer compound which possesses a hydroxyl group. Copolymers which include the monomers listed below and the molecular weights of which normally range from 5,000 to 200,000 may, for example, be used as such a lipophilic polymer compound which possesses a hydroxyl group and which can be used for said purpose:

(1): Monomers which possess aromatic hydroxyl groups such as N- (4-hydroxyphenyl)acrylamide or N- (4-

hydroxyphenyl)methacrylamide, o-, m-, and/or p-hydroxystyrene, o-, m-, and/or p-hydroxyphenyl acrylate or methacrylate; and

(2): Monomers which possess aliphatic hydroxyl groups such as 2-hydroxyethyl acrylate or 2-hydroxyethyl methacrylate.

Other monomers which can be copolymerized include

(1): α, β -unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic anhydride, etc.;

(2): (Substituted) alkyl acrylates such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, hexyl acrylate, octyl acrylate, 2-chloroethyl acrylate, 2-hydroxyethyl acrylate, glycidyl acrylate, N-dimethylaminoethyl acrylate, etc.;

(3): (Substituted) alkyl methacrylates such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, amyl methacrylate, cyclohexyl methacrylate, 2-hydroxyethyl methacrylate, 4-hydroxybutyl methacrylate, glycidyl methacrylate, N-dimethylaminoethyl methacrylate, etc.;

(4): Acrylamides or methacrylamides such as acrylamide, methacrylamide, N-methylolacrylamide, N-methylolmethacrylamide, N-ethylacrylamide, N-hexylmethacrylamide, N-cyclohexylacrylamide, N-hydroxyethylacrylamide, N-phenylacrylamide, N-nitrophenylacrylamide, N-ethyl-N-phenylacrylamide, etc.;

(5): Vinyl ethers such as ethyl vinyl ether, 2-chloroethyl vinyl ether, hydroxyethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, octyl vinyl ether, phenyl vinyl ether, etc.;

(6): Vinyl esters such as vinyl acetate, vinyl chloroacetate, vinyl butyrate, vinyl benzoate, etc.;

(7): Styrenes such as styrene, α -methylstyrene, methylstyrene, chloromethylstyrene, etc.;

(8): Vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone, propyl vinyl ketone, phenyl vinyl ketone, etc.;

(9): Olefins such as ethylene, propylene, isobutylene, butadiene, isoprene, etc.; and

(10): N-vinylpyrrolidone, N-vinylcarbazole, 4-vinylpyridine, acrylonitrile, methacrylonitrile, etc., although it is also possible select other monomers so long as they can be copolymerized with the hydroxyl group-containing monomers, and thus, the foregoing examples are not binding. If necessary, furthermore, it is also possible to add a polyvinyl butyral resin, polyurethane resin, polyamide resin, epoxy resin, novolak resin, natural resins, etc.

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The internalization ratio of the lipophilic polymer compound in possession of a hydroxyl group with respect to the solid content of the photosensitive composition is normally designated within a range of 1 ~ 99 wt%, preferably 5 ~ 95 wt%. The internalization ratio of the diazo resin, furthermore, is normally designated within a range of 1 ~ 100 wt%, preferably 5 ~ 90 wt%.

The performances of the photosensitive component of the present invention may be further improved by adding the various conventionally-known additives shown below to it:

(1): Dyes added for the purpose of visualizing images;

(2): Fluorinated surfactants or alkyl ethers added for the purpose of improving the coatability;

(3): Plasticizers added for the purpose of conferring flexibility and abrasion resistance on the coating film;

(4): Liposensitizing agents;

(5): Stabilizers.

Their addition ratios with respect to the total solid content are generally designated within a range of 0.01 ~ 30 wt%.

The photosensitive composition of the present invention is coated on the substrate of the present invention after having been solubilized into an appropriate solvent (e.g., methyl Cellosolve, methyl ethyl ketone, ethyl Cellosolve, cyclohexanone, dioxane, ethyl acetate, benzyl alcohol, diacetone alcohol, etc.).

The coating rate is normally designated within a range of approximately 0.5 ~ 5 g/m² in terms of the dry weight standard. The aluminum sheet of the present invention is subjected to an anodic oxidation treatment within phosphoric acid or an electrolytic solution inclusive of phosphoric acid as a main component. The aluminum sheet may, for example, be used after having been anodically oxidized within an aqueous solution which includes 10 ~ 50 wt%, preferably 20 ~ 40 wt%, of phosphoric acid or an aqueous mixed acid solution which includes, in addition to said phosphoric acid, no more than 25 wt%, preferably no more than 10 wt%, of another acid(s) (e.g., sulfuric acid, oxalic acid, etc.) with respect to the total acid content at a bath temperature of 10 ~ 50°C, preferably 25 ~ 45°C, at a current density of 0.2 ~

10 A/dm², preferably 1 ~ 7 A/dm², and over a duration of 10 sec. ~ 10 min., preferably 20 sec. ~ 3 min., in such a way that the average pore diameter of the obtained anodic oxidation layer will be 200 ~ 900 Å, preferably 300 ~ 900 Å, and that the pore density of the same will be 100 ~ 1,000 N/μm², preferably 100 ~ 500 N/μm². It is desirable for the aluminum sheet of the present invention to be subjected, before or after the anodic oxidation treatment, to a surface treatment based on a conventionally-known method (e.g., brush polish, sandblasting treatment by means of electrolytic etching, etc., and/or hydrophilicizing treatment, etc.).

A hot water pore sealing treatment or sodium silicate treatment is conceivable as said hydrophilicizing treatment, although the sodium silicate treatment is the more desirable in consideration of the adhesion compatibility, diazo residue ratio, and developability. As far as the conditions of the sodium silicate treatment are concerned, an immersion within a sodium silicate solution with a concentration of 0.1 ~ 5% is executed within a temperature range of 50°C ~ 95°C for 10 sec. ~ 5 min. It is desirable for the treated object to be further immersed in and treated with water at 60°C ~ 100°C for 10 sec. ~ 5 min.

An image is encoded into the photosensitive planographic printing plate thus manufactured by exposing it via a laminated photographic subject or by instead irradiating electron beams, etc., and in a case where a development operation is then carried out by using a development solution, a corresponding image can be formed on the substrate. Light sources used favorably for

exposure are instantiated by a metal halide lamp, mercury lamp, carbon arc lamp, etc.

In the following, examples for manufacturing substrates and diazo resins to be used in the present invention will be shown.

(Substrate 1)

After an aluminum sheet had been subjected to an electrolytic polishing treatment within a 17 g/L hydrochloric acid bath at a bath temperature of 25°C and at 50 A/dm² for 25 sec., a sandblasted sheet with a maximal roughness of 4 μm was obtained. After said sandblasted sheet had been subjected to an anodic oxidation treatment within a 40 wt% phosphoric acid bath at a bath temperature of 40°C at 4 A/dm² for 30 sec., it was sufficiently washed with water and then dried with air. In a case where the obtained anodic oxidation layer was analyzed by using an electron microscope, 175 N/ μm^2 pores with an average pore diameter of 750 Å were verified.

(Substrate 2)

An aluminum sheet which had been sandblasted according to procedures similar to those for Substrate 1 was subjected to an anodic oxidation treatment within a mixed acid bath inclusive of 30 wt% of phosphoric acid and 25 wt% of sulfuric acid at a bath temperature of 40°C and at 4 A/dm² for 30 sec., sufficiently washed with water, and then dried with air. In a case where the obtained

anodic oxidation layer was analyzed by using an electron microscope, $220 \text{ N}/\mu\text{m}^2$ pores with an average pore diameter of 500 \AA were verified. /8

(Substrate 3)

It was verified that $350 \text{ N}/\mu\text{m}^2$ pores with an average pore diameter of 350 \AA had been formed on an anodic oxidation layer which had been treated within a mixed acid bath inclusive of 30 wt% of phosphoric acid and 5 wt% of sulfuric acid under conditions otherwise identical to those for Substrate 2.

(Substrate 4)

It was verified that $1,000 \text{ N}/\mu\text{m}^2$ pores with an average pore diameter of 250 \AA had been formed on an anodic oxidation layer which had been treated within a mixed acid bath inclusive of 30 wt% of phosphoric acid and 30 wt% of sulfuric acid under conditions otherwise identical to those for Substrate 2.

(Substrate 5)

An aluminum sheet which had been sandblasted according to procedures similar to those for Substrate 1 was subjected to an anodic oxidation treatment within a 30 wt% sulfuric acid bath at a bath temperature of 30°C and at $6 \text{ A}/\text{dm}^2$ for 30 sec., sufficiently washed with water, and then dried with air. In a case where the obtained anodic oxidation layer was analyzed according to

procedures similar to those in Reference Example 1 [sic], 1,000 N/ μm^2 pores with an average pore diameter of 130 Å were verified.

(Substrate 6)

It was verified that at least 1,000 N/ μm^2 pores with an average pore diameter of 80 Å had been formed on an anodic oxidation layer which had been obtained at a current density of 4 A/dm² under conditions otherwise identical to those for Substrate 5.

(Substrate 7)

It was verified that at least 100 N/ μm^2 pores with an average pore diameter of 950 Å had been formed on an anodic oxidation layer which had been obtained at a current density of 9 A/dm² under conditions otherwise identical to those for Substrate 1.

(Diazo Resin 1)

29.6 g (0.1 mole) of the zinc salt of 4-(N-ethyl-N-hydroxyethyl)-aminobenzene diazonium chloride and 19.6 g (0.12 mole) of ammonium hexafluorophosphate were mixed with one another in an ice cooled state within 200 mL of water, as a result of which 28 g of the hexafluorophosphate of the diazo species was obtained. 6.7 g (0.02 mole) of this diazo hexafluorophosphate, 11.4 g (0.02 mole) of a styrene/maleic anhydride (1/1) copolymer ("Styrite CM-2L," manufactured by Sankyo Kasei Co.; weight-based average molecular weight: 5,000), and 70 mg (0.0004 mole) of p-

toluenesulfonic acid were solubilized into 80 mL of acetone, and after the contents had been agitated at room temperature over a 3-hour period, the obtained mixture was left unattended overnight.

This solution was added dropwise to 2 L of water, and after the generated precipitate had been filtered and washed with water, it was dried overnight at 30°C, as a result of which Diazo Resin 1 was obtained. It was verified by means of IR that the maleic anhydride segment of Diazo Resin 1 had been completely decycled and half esterified.

(Diazo Resin 2)

5 g (25.3 mmole) of a copolymer of methyl methacrylate and maleic anhydride (1 : 1) (weight-based average molecular weight: 8,200), 8.5 g (25.3 mmole) of the diazo hexafluorophosphate mentioned in Synthesis Example 1 [sic], and 87 mg (0.51 mmole) of p-toluenesulfonic acid were solubilized into 80 mL of acetone, and after the contents had been agitated at room temperature over a 3-hour period, it was left unattended overnight.

This solution was added dropwise to 2 L of water, and after the generated precipitate had been filtered and washed with water, it was dried overnight at 30°C, as a result of which Diazo Resin 2 was obtained.

It was verified by means of IR that the maleic anhydride segment of Diazo Resin 2 had been completely decycled and half esterified.

(Diazo Resin 3)

35.8 g (0.1 mole) of the zinc salt of 4-(N-benzyl-N-hydroxyethyl)-aminobenzene diazonium chloride and 36.8 g (0.12 mole) of 2-oxy-4-methoxybenzophenone-5-sulfonic acid were mixed with one another in an ice cooled state within 200 mL of water, as a result of which 50 g of the 2-oxy-4-methoxybenzophenone-5-sulfonate of the diazo species was obtained. Operative procedures similar to those for Diazo Resin 1 were subsequently carried out (though CM2L as polymer), as a result of which Diazo Resin 3 was obtained.

It was verified by means of IR that the maleic anhydride segment of Diazo Resin 3, too, had been completely decycled and half esterified.

(Diazo Resin 4)

35.6 g (0.1 mole) of the zinc salt of 2,5-dimethoxy-4-[-(N-ethyl-N-hydroxyethyl)-^{/9}amino}benzene diazonium chloride and 36.8 g (0.12 mole) of 2-oxy-4-methoxybenzophenone-5-sulfonic acid were mixed with one another in an ice cooled state within 200 mL of water, as a result of which 55 g of the 2-oxy-4-methoxybenzophenone-5-sulfonate of the diazo species was obtained. Operative procedures similar to those for Diazo Resin 1 were subsequently carried out (though CM-2L as polymer), as a result of which Diazo Resin 4 was obtained.

(Application examples)

In the following, the present invention will be explained more concretely with reference to application examples, although the present invention is not limited to these application examples.

Application Examples 1 ~ 4 and Comparative Examples 1 ~ 3

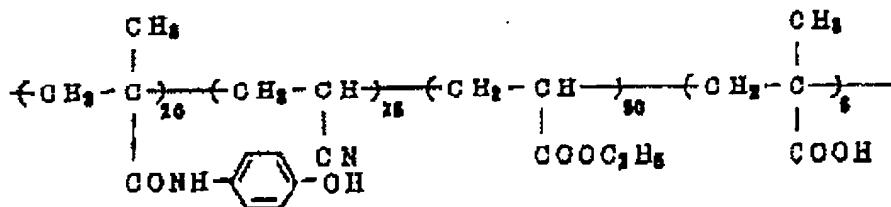
Photosensitive Solution 1, the composition of which is shown below, was coated on each of Substrates 1 ~ 7 obtained in the aforementioned production examples by using a whaler, and after it had been dried at 80°C over a 3-min. period, a photosensitive planographic printing plate was obtained. The coating rate was 1.0 g/m² by the dry weight standard.

(Photosensitive Solution 1)

Diazo Resin 1: 5 g; Polymer 1*: 5 g; Victoria Pure Blue BCH (manufactured by Hodogaya Chemical Co.): 0.2 g; methyl Cellosolve: 200 mL.

The obtained photosensitive planographic printing plate was exposed to a 3 KW ultra-high-pressure mercury lamp at a distance of 80 cm over a 1-min. period, and after its exposure image visualization capacity had been measured, it was developed by using Development Solution 1 shown below, as a result of which a planographic printing plate was obtained.

*: The weight-based average molecular weight of Polymer 1, the composition of which is shown below, was 80,000.



(Development Solution 1)

Benzyl alcohol: 10 g; triethanolamine: 3 g; sodium sulfite: 1 g; sodium butylnaphthalenesulfonate: 5 g; water: 1,000 g.

The sensitivity, dot blot margin, printing force resistance, and preservation stability of the obtained planographic printing plate were measured. The obtained results are shown in Table I.

The exposure image visualization capacity was evaluated by measuring the reflective density differential between image and non-image segments by using a Macbeth reflective densitometer (visual filter), and a value of at least 0.25 was judged to be "favorable," whereas "unacceptable" was judged in a case where it was lower than 0.25.

The sensitivity was judged by the naked eye in terms of the plain print step No. of step wedge steps.

The dot blot margin was measured in terms of the dot blot margin of a 150 line/inch 55% original.

The preservation stability was judged in terms of the presence or absence of non-image segment stains after a 3-day preservation period at a temperature of 40°C and at a humidity of 90%. The printing force resistance was evaluated by printing a rolled paper by using an offset rotary printer, and the printed copy number at which a flat net scratch or plainly printed segment

defect had occurred was defined as the printing force resistance.

Table I

/10

	AE 1	AE 2	AE 3	AE 4	CE 1	CE 2	CE 3
(A)	SB 1	SB 2	SB 3	SB 4	SB 5	SB 6	SB 7
(B)	H ₂ SO ₄	H ₂ PO ₄ /H ₂ SO ₄	←	←	H ₂ SO ₄	←	H ₂ PO ₄
(C)	750	500	350	250	130	80	950
(D)	175	220	350	1000	> 1000	> 1000	100
(E)	5	5	5½	4½	4	4½	5½
(F)	4.1	3.5	4.2	6.0	12.0	11.5	8.0
(G)	> 20	> 20	> 20	> 15	5	3	> 20
(H)	(K)	(K)	(K)	(K)	(K)	(K)	(K)
(I)	(K)	(K)	(K)	(K)	(K)	(K)	(L)
(J)	(K)	(K)	(K)	(K)	(K)	(K)	(M)

[(AE) : Application Example; (CE) : Chlorine; (SB) substrate; (A) : No.; (B) : Anodic oxidation electrolytic solution; (C) : Average pore diameter (Å); (D) : Pore density (N/μm²); (E) : Sensitivity (step wedge step No.); (F) : Dot blot margin (5-th step equivalent)]

(%) ; (G) : Printing force resistance (x 10,000 copies); (H) : Exposure image visualization capacity; (I) : Preservation stability; (J) : Erasability; (K) : Favorable; (L) : Unacceptable; (M) : Defective]

It can be inferred from Table I that the exposure image visualization capacity and image reproducibility of the photosensitive planographic printing plate of the present invention are excellent, that its preservation stability and erasability are also excellent, and that its printing force resistance is extremely favorable.

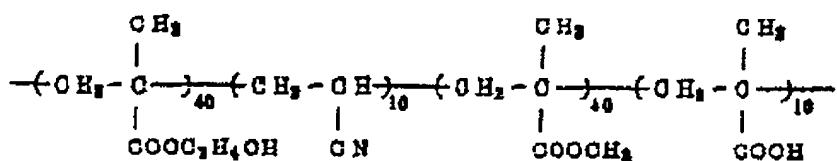
Application Examples 5 ~ 8

Photosensitive Solution 2, the composition of which is shown below, was coated on Substrate 2 by using a whaler, and after it had been dried at 80°C over a 3-min. period, a photosensitive planographic printing plate was obtained. The coating rate was 1.5 g/m² by the dry weight standard.

(Photosensitive Solution 2)

Polymer 2^{**}: 8 g; Diazo Resins 1 ~ 4: 2 g; Oil Blue #603 (manufactured by Orient Chemical Co.): 0.4 g; methyl Cellosolve: 200 mL.

**: The weight-based average molecular weight of Polymer 2, the composition of which is shown below, was 40,000.



After the obtained photosensitive planographic printing plate had been left unattended underneath a white beam lamp over a 3-hour period, it was exposed and developed, as a result of which a planographic printing plate was obtained. After the obtained planographic printing plate had been mounted on a GTO printer (manufactured by Heidelberg Co.), a printing operation was carried out, as a result of which the results shown in Table II were obtained. Moreover, the printing force resistance was investigated, and the obtained results are also shown in Table II.

Comparative Example 4

Photosensitive Solution 3 was prepared according to procedures identical to those for preparing Photosensitive Solution 2 except that the diazo resin of the latter was substituted with the PF_6^- salt of a condensation product of *p*-diazodiphenylamine and formaldehyde (GPC molecular weight measurement revealed that approximately 35 mol% of trimer and more advanced components were included), and after it had been coated on Substrate 2 according to procedures similar to those in Application Examples 5 ~ 8 by using a whaler, it was dried, as a result of which a photosensitive planographic printing plate was obtained.

After it had been left unattended underneath a white beam lamp (500 lux) over a 1-hour period, as in Application Examples 5 ~ 8, it was exposed and developed, as a result of which a planographic printing plate was obtained.

It was used for printing according to procedures similar to those in Application Examples 5 ~ 8, and the obtained results are shown in Table II.

Table II

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	AE 5	AE 6	AE 7	AE 8	CE 4
(A)	1	2	3	4	(D)
(B)	(E)	(E)	(E)	(E)	(F)
(C)	> 30	> 30	> 30	> 30	20

[(AE) : Application Example; (CE) : Comparative Example; (A) : Diazo resin; (B) : Stains of non-image segments after having been left unattended underneath a white beam lamp; (C) : Printing force resistance (x 10,000 copies); (D) : PF₆ salt of condensation product of p-diazodiphenylamine and formaldehyde; (E) : Absent; (F) : Present]

It can be inferred from Table II that the photosensitive planographic printing plate of the present invention is unaccompanied by base stains even in a case where it is handled under a white beam lamp and that its printing force resistance is extremely favorable as well.

(Effects of the invention)

As the foregoing explanations have demonstrated, remarkable effects can be achieved by the photosensitive planographic printing plate of the present invention in that it is endowed with an extremely favorable and high printing force resistance, excellent preservation stability & erasability, and excellent exposure image visualization potential & image reproducibility and that it is unaccompanied by a fog even in a case where it is handled underneath a white beam lamp.